

IONIZATION OF CHLORINE AND IODINE IN FUSED SALTS

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IONIZATION OF CHLORINE AND IODINE IN FUSED SALTS

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ABSTRACT

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Chlorine ionization was studied with carbon and graphite electrodes; iodine was studied on a tungsten electrode. It is found that the current increase on the tri-phase boundary is related to the diffusion increase through the thin layer of melt. *AUTHOR*

An investigation of haloid ionization in fused salts is of interest /709* with respect to the development of studies on high-temperature heat cells, in which a haloid is employed as the oxidizer (Ref. 1). At large loadings, the current output from the electrodes is determined by the haloid ionization rate. Therefore, a detailed study of this reaction must be of assistance in developing unpolarized gas electrodes for this type of heat cell.

This article describes the results derived from studying the ionization reaction of chlorine and iodine. Chlorine ionization was studied with carbon and graphite electrodes. Electrodes made of pyrolytic graphite were employed; this is an almost nonporous material. The ionization reaction of iodine was studied on a tungsten electrode, which is inert with respect to iodine at high

* Note: Numbers in the margin indicate pagination in the original foreign text.

temperatures (Ref. 2). The following salts were employed as the electrolytes: silver chloride, lead chloride, an eutectic mixture of lithium chloride and potassium chloride. Iodine ionization was studied in the melt of a lead iodine salt.

The ionization of chlorine and iodine was studied in a two-electrode element. It follows from (Ref. 3) that the liberation of chlorine and iodine from melts of their salts in graphite occurs without overvoltage - at least /710 up to currents on the order to 10 a/cm^2 . We found that there is no chemical polarization during the liberation of chlorine in special experiments in a three-electrode element. Based on this fact, in a two-electrode element - when both electrodes are located in an atmosphere of chlorine or iodine - the polarization of the element is related to the polarization of the cathode and the ohmic voltage decrease when a current is passed through. Based on the voltage decrease after the current was shut off, which was recorded by means of an oscillograph, it was found that in our case at current densities up to 10^{-2} a/cm^2 the polarization component, which is related to the ohmic electrolyte resistance, represents an insignificant portion of the total polarization.

Figure 1 shows a drawing of the device employed in the experiments on the ionization of chlorine. The electrodes to be studied were in the form of thin rods having a diameter of 2 mm. The lower electrode made of pyrolite graphite was sealed into a Pyrex tube, whose upper portion was filled with the fused salt. As a result of employing this construction, the lower electrode could operate as an electrode which did not have a three-phase boundary. The upper electrode was interchangeable, and in addition the height of its immersed section could be changed during the experiment.

The device shown in Figure 2 was employed in experiments on iodine /711

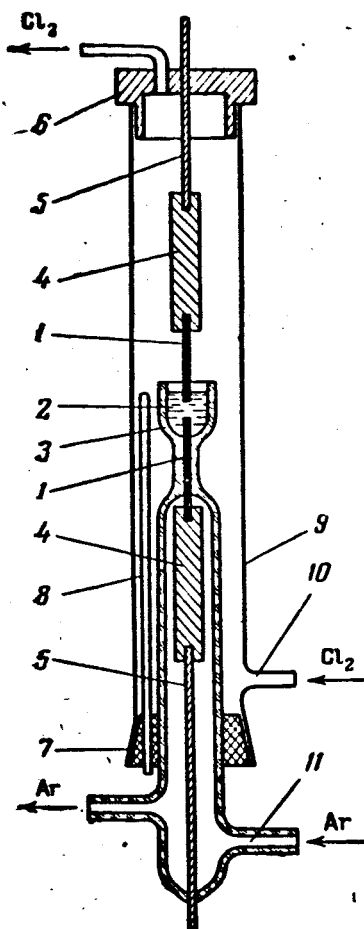


Figure 1

Device for Chlorine Ionization

1 - Electrodes to be studied; 2 - Fused salts; 3 - Pyrex beaker for the melt; 4 - Graphite rods; 5 - Tungsten leads; 6 - Teflon stopper; 7 - Rubber stopper; 8 - Container for thermocouple; 9 - Quartz housing; 10 - Lead for chlorine; 11 - Lead for argon

ionization. It was a Pyrex tube with two tungsten seals. The salt, a portion of iodine which would have to produce a pressure equalling one atmosphere at a temperature of 500°C, was placed in the tube. The device was evacuated with a fore pump and sealed off under a vacuum.

The current-potential curves were recorded by means of an oscillographic

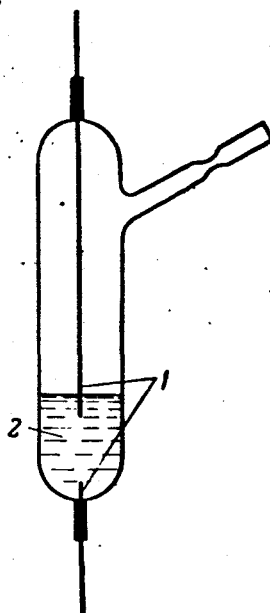


Figure 2

Device for Iodine Ionization

1 - Tungsten electrodes; 2 - Fused salt

OP-1-61 polarograph; small changes were made in it due to the necessity of operating with currents on the order of several milliamperes. In the experiments described in this article, the rate at which the potential applied to the electrodes was changed, was 0.1 v/sec.

Figure 3 shows typical curves for chlorine ionization on a carbon electrode in a AgCl melt recorded at different temperatures. Similar curves were also obtained for the melt of the eutectic mixture KCl + LiCl on a carbon electrode. It must be noted that the reproducibility of curves for silver chloride is better than for the eutectic. One characteristic of a carbon electrode is the absence of a maximum current area at rather high cathode potentials. It is difficult to explain the mechanism by which the carbon electrode operates on

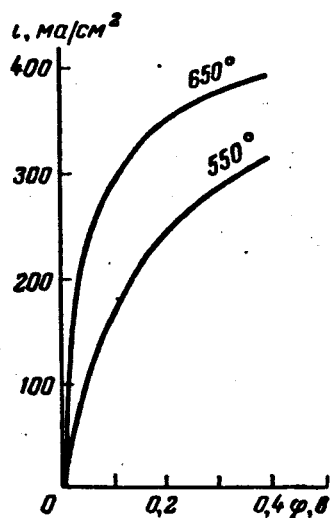


Figure 3

Curves Showing Dependence of Current Density on Potential in a Melt of AgCl Salt at Different Temperatures on a Carbon Electrode

the basis of the ionization curves recorded for it, due to the complex and rather uncertain structure of the tri-phase boundary. A certain amount of light can be thrown on this subject by studying the ionization process on almost non-porous pyrolitic graphite.

Figure 4 shows the curves for the current-potential density recorded for a completely immersed electrode made of pyrolitic graphite for the melts of the AgCl, PbCl₂ and KCl + LiCl salts. Figures 5 and 6 show the dependence of the current density on potential on an electrode with a tri-phase boundary for melts of the AgCl and KCl + LiCl salts. The curves obtained for a completely immersed electrode have a small maximum current area (curve 1). Curves recorded for an electrode with a boundary (curve 2) have current values which are somewhat greater than for fully-immersed electrodes. This indicates that the thin layer, adjacent to the electrode, of the melt on the tri-phase boundary plays a certain role. In contrast to aqueous solutions (Ref. 4), in which the electrode

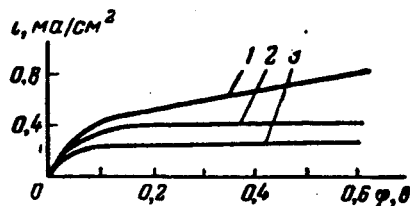


Figure 4

Curves Showing Dependence of Current Density on Potential on a Pyrolytic Graphite Electrode at a Temperature of 520°C in Melts of Different Salts: 1 - PbCl_2 ; 2 - AgCl ; 3 - $\text{LiCl} - \text{KCl}$

is moistened by the electrolyte - forming thin films which are rather extended, and which play a large role in the current formations on the porous electrodes - the AgCl melt does not wet the graphite, as can be seen from the following considerations, in contrast to the melts of alkali and alkali earth metal salts (Ref. 5). Probably, the current increase is related to the operation of the thin layer of melt on the tri-phase boundary, through which intense diffusion of chlorine takes place. /712

The assumption that the current increase on the tri-phase boundary is related to the diffusion increase through the thin layer of melt, and not to the rapid diffusion of chlorine along the electrode surface, is substantiated by the following experiment. The electrode to be studied was carefully immersed to a certain depth in the melt. The curves thus recorded (Figure 5) for the current magnitude only slightly exceeded the currents for a fully immersed electrode, while the currents increased by almost one order of magnitude after the electrode was carefully pulled out a small distance (Figures 5, 6, curve 3). Light tapping on the electrode (for experiments in a AgCl melt) led to a current decrease down to the initial value when it was

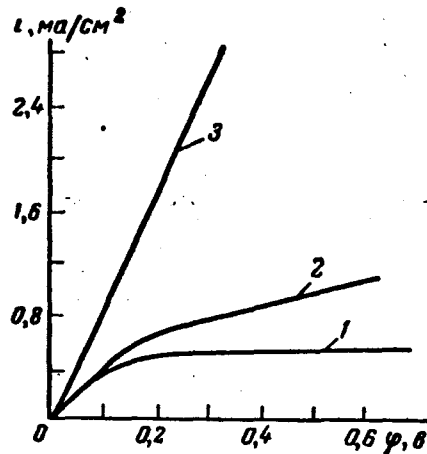


Figure 5

Curves Showing Dependence of Current Density on Potential in the LiCl - KCl Eutectic Melt at a Temperature of 570°C on Pyrolytic Graphite Electrodes.

immersed. This can be explained by the fact that, when the electrode was pulled out of the melt, a film was formed due to mechanical adhesion with the surface irregularities. This film led to a current increase, but it readily decreased when the electrode was shaken. A bulging meniscus was formed on the melt-electrode boundary.

Curves showing the density of the current-potential (Figure 7) for iodine ionization were recorded for fully immersed electrodes and for partially immersed electrodes made of tungsten in a PbJ_2 salt melt.

It can be seen from Figure 7 that for iodine, just as for chlorine, the presence of the tri-phase boundary leads to a current increase. The magnitude of the maximum currents is one order of magnitude greater for iodine than it is for chlorine in a PbCl_2 melt at the same temperatures. This relative increase in the maximum current can be explained by the greater solubility of

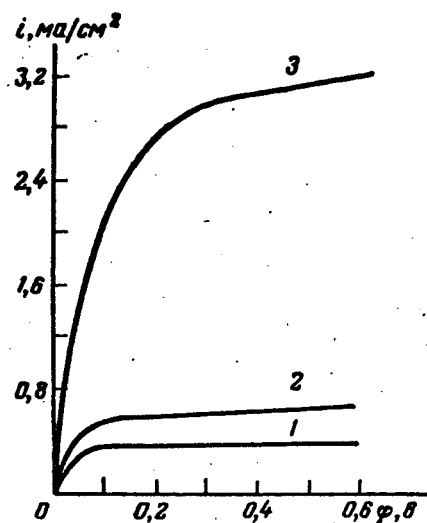


Figure 6

Curves Showing Dependence of Current Density
on Potential in a AgCl Salt Melt at a
Temperature of 600°C on Pyrolytic
Graphite Electrodes.

iodine in a melt of its salt than that of chlorine.

Comparing currents obtained during ionization of chlorine on a carbon /713 electrode and on an electrode made of pyrolytic graphite, one can see that they differ by a factor of 100. Taking the fact into account that the fused salt of AgCl does not wet the carbon, and consequently does not fill the electrode pores, we can see that the surface where the melt contacts the porous electrode can not be increased by two orders of magnitude, due to an increase in the roughness of the carbon working surface, as compared with the graphite electrode. In this case, there is a current increase which can probably be explained by an increase in the tri-phase boundary length, which is greater than 100 cm per cm² for carbon.

As can be seen from Figure 5, if the current increase due to the formation

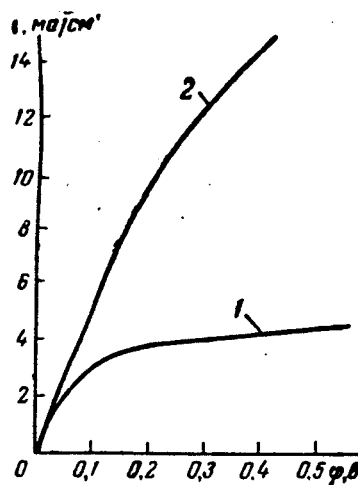


Figure 7

Curves Showing Dependence of Current Density on Potential in a PbJ_2 Melt at a Temperature of 500°C for Tungsten Electrodes.

of a tri-phase boundary with a length of 5 mm is 30-50% of the current for a fully immersed electrode equalling 0.4 ma/cm^2 , then the simple increase in the tri-phase boundary may explain the observed values for currents on a carbon electrode. For a $\text{KCl} - \text{LiCl}$ eutectic, the operation of the carbon electrode is complicated by the wettability of the carbon by the melt in connection with the "Wetting" of the electrode, which probably explains the time changes in its polarization characteristic.

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